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COMPOSITE ALUMINUM OXIDE CERAMICS WITH FIBROUS COMPONENTS

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The reactions between oxides in the $Al_2O_3 – ZrO_2 – MgO$ system in the production of ceramics using fibrous components are studied. It is established that under heat treatment of the ternary systems, the component stabilizing the tetragonal structure of zirconium dioxide reacts with the aluminum oxide matrix and forms spinel interlayers on the fiber – matrix interface. The use of highly disperse fibers as the initial component for producing ceramics and as a fibrous filler additive introduced into a gel-like matrix makes it possible to obtain composite ceramics of elevated strength.

Contemporary engineering calls for new strengthened heat- and corrosion-resistant ceramic materials. Heat-resistant ceramics with high mechanic parameters are produced from mixtures of aluminum oxide and stabilized zirconium dioxide [1]. However, the solid solutions of zirconium dioxide in ceramics of the triple $Al_2O_3 – ZrO_2 – MgO$ composition produced from a melt or by oxide powder sintering completely disintegrate at temperatures above 1500°C and a monoclinic phase is formed, which impairs the strength properties of the material [2]. At the same time it is known that in transition from a macrostructure to nanosized microstructures, the processes and properties of the material are substantially modified [3]. Considering that powders produced by the sol-gel method have high dispersion and that oxide fibers consist of nanosized particles, one can suppose that composite materials containing such components have specific properties.

The present study is dedicated to studying the reactions of oxides in the production of composite ceramics of the $Al_2O_3 – ZrO_2 – MgO$ composition using fibrous components and their effect on the structure and properties of ceramic materials.

Two main methods were used in the production of the ceramics.

In the first method, three-component fibers were synthesized with different ratios of $Al_2O_3 : ZrO_2 : MgO$; the first mixture had the ratio of 98.5 : 1.0 : 0.5, the second mixture 93.0 : 5.0 : 2.0, and the third mixture 87.5 : 10.0 : 2.50, respectively. The resulting fibers were milled, screened by fractions, molded in the shape of bars $5 \times 5 \times 50$ mm and cylinders of diameter 10 mm and height 15 – 20 mm using a temporary binder, and heat-treated in an oxidizing atmosphere at preset temperatures.

The second method of obtaining three-component compositions included a stage of precipitation of aluminum hydroxide gel from an aqueous solution of aluminum chloride by means of ammonium solution and the simultaneous introduction of a fibrous powder of partly stabilized (by means of magnesium oxide) zirconium oxide into the gel. The quantity of the fiber introduced varied from 5 to 20 wt.% with respect to aluminum oxide. The obtained precipitate containing the fiber was washed, dried, and molded in the form of cylinder and bars of the sizes specified above. The annealing was performed in air within a temperature range of 100 – 1600°C with an interval of 100°C, and the weight loss and shrinkage of the samples were measured after annealing.

The processes taking place in heating were studied using a MOM derivatograph of the Paulik – Paulik – Érdey system. The material was heated in corundum crucibles, the rate of temperature rise varied from 2 to 10 K/min, the portion of material weighed 500 – 800 mg, and the reference sample was made of aluminum oxide annealed at a temperature of 1200°C.

The physicomechanical properties of ceramics were determined by the standard methods: the strength properties were tested by the three-point bending method on an Instron-1195 M universal testing machine with a precision of measuring the ultimate breaking load equal to 1%. The material structure was studied using a DRON-3 diffraction analyzer, the diffraction patterns were recorded in the angle interval 2θ from 5 to 110 deg, using monochromatic CuK_α radiation (wavelength 0.154 nm), and the data were processed on a computer. The surfaces of ceramic sample fractures were

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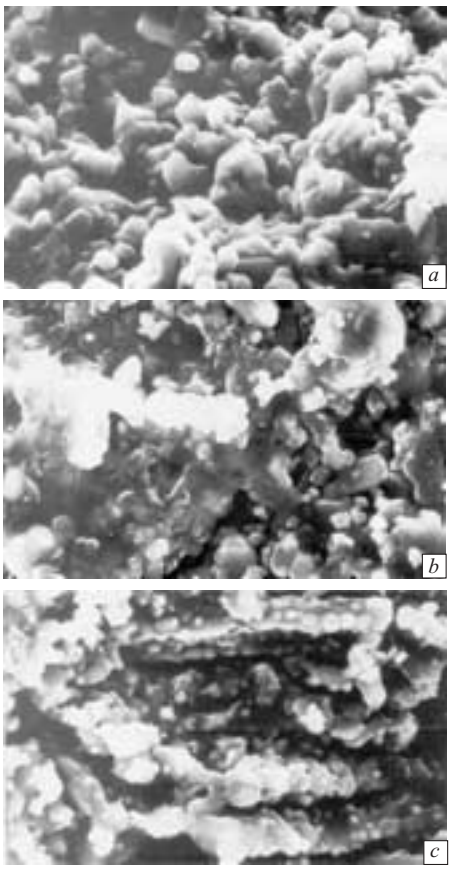

Fig. 1. Microstructure of ceramics annealed at 1600°C based on the first (*a*), second (*b*), and third (*c*) mixtures.

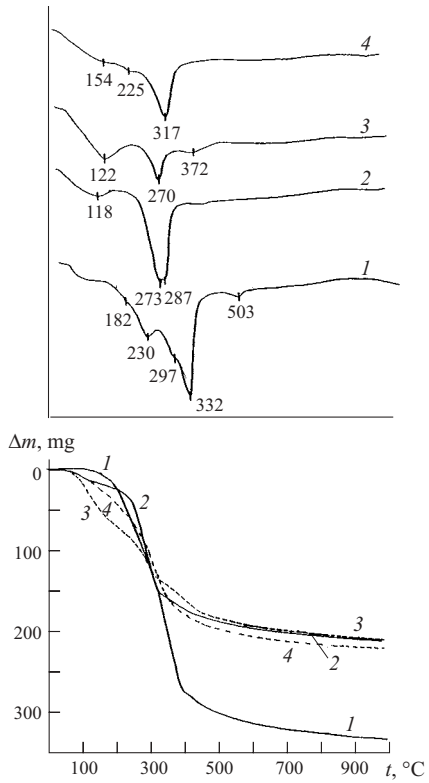

Fig. 2. DTA and TG curves of hydroxide aluminum gel (*1*) and composites with partly stabilized zirconium dioxide with a filler content of 5 (*2*), 15 (*3*), and 20% (*4*).

studied with a JSM-35 (JEOL) scanning electron microscope at a magnification of 500 – 20,000.

Ceramics made from fibrous powders. Samples produced by the first method were annealed, measured, and the weight loss and shrinkage were determined. After heat treatment at 1100°C the weight loss of ceramic samples of the first and the second mixtures was equal to 11.5%, and in the third mixture it was slightly higher (14.2%). After annealing at 1600°C the weight losses were 13.5 and 15.5%, respectively. The sintering processes in the ternary system at 1100°C were insignificant in all three mixtures, and the shrinkage of the bars in length, width, and weight was equal to 6.0, 4.2, and 6.1%.

According to the x-ray data, the crystalline structure of the initial fibrous powders was characterized by the presence of two phases (γ- and θ-) of aluminum oxide and the tetragonal phase of zirconium dioxide. Modifications in the crystalline structure of the three-component ceramics occurred within a temperature range of 1100 – 1600°C. When heated to 1100 – 1200°C, the γ- and θ-phases of aluminum oxide were transformed into α-corundum, and the reflections of aluminum-magnesium spinel were registered on the diffraction patterns at a temperature over 1300°C. It should be noted that the spinel formation was accompanied by partial decomposition of the solid solution of zirconium dioxide. However, the content of the monoclinic phase was insignificant in ratio to the introduced ZrO_2 and amounted to 2% in the samples of the second mixture and 4% in the ceramic based on the third mixture. No monoclinic phase was observed in the samples based on the first composition.

An electron microscope study of sample fractures revealed that the fibrous texture of ceramic persisted under heat treatment up to 1400°C. At a temperature over 1600°C, a heterogeneous structure consisting of fiber fragments and spherical particles emerged in the ceramics, and as the content of zirconium dioxide increased (the third mixture), more extended fragments, bridges, and arches were registered in ceramics (Fig. 1). The compressive strength of the samples grew with an increasing content of zirconium dioxide: in the ceramics of the third mixture it amounted to 650 MPa and the three-point bending strength was 340 MPa.

Ceramics produced by the sol-gel method. The use of fiber to reinforce composite materials has been described [4, 5] earlier. The quantity of the filler for composite materials is usually selected based on calculations or additional experiments. For this purpose we prepared samples made from pure aluminum hydroxide gel and from composites containing from 5 to 20 wt.% fiber additive of partly stabilized (by magnesium oxide) zirconium dioxide. A study of the process of obtaining gel precipitate with fibrous fillers, which have

an extended surface, a high porosity, and consist of nanosized oxide grains, established that aqueous complexes are formed on the fiber surface at the moment of hydrated aluminum-oxide gel precipitation; these complexes lose water under heat treatment and form solid solutions and compounds at the fiber – matrix interface. Such phenomenon was earlier observed in producing composite materials from hydrated zirconium dioxide gel with aluminum oxide fibers [6].

According to the data of differential thermal analysis, adsorbed, crystallization, and interlayer water was removed from pure aluminum hydroxide in heating at temperatures of 80 – 100, 230, and 297°C, respectively. Within a temperature range of 300 – 350°C, aluminum hydroxide decomposed and γ-Al_2O_3 was formed, which under further heating transformed into the θ-phase and at 1150°C transformed into α-corundum. A 5% additive of zirconium dioxide fibers stabilized by magnesium oxide modified the process of $Al(OH)_3$ dehydration and the cubic structure of aluminum oxide crystallized at 400°C. An increase to 20% in the fiber content in the aluminum hydroxide gel not only modified the whole process of dehydration but also retarded the crystallization of aluminum oxide, which was formed as the γ-phase, to a temperature of 700°C (Fig. 2).

TABLE 1

Temperature, °C	Phase	
	pure Al_2O_3 gel	composite with ZrO_2 fiber
100	$Al(OH)_3$ (α-, β- and triclinic phases)	$ZrO_2(t) + ZrO_2(m) + Al(OH)_3$ (β- and triclinic phases)
200	The same	The same
300	γ-Al_2O_3	$ZrO_2(t) + ZrO_2(m)$
400	The same	The same
500	″	″
600	″	″
700	γ-Al_2O_3 + δ-Al_2O_3 + θ-Al_2O_3	$ZrO_2(t) + ZrO_2(m) + \gamma$-$Al_2O_3$
800	γ-Al_2O_3 + θ-Al_2O_3	$ZrO_2(t) + ZrO_2(m) + \gamma$-$Al_2O_3$ + θ-Al_2O_3
900	The same	The same
1000	θ-Al_2O_3	″
1100	θ-Al_2O_3+α-Al_2O_3	$ZrO_2(t) + ZrO_2(m) + \alpha$-$Al_2O_3$ + θ-Al_2O_3
1200	α-Al_2O_3	$ZrO_2(t) + ZrO_2(m) + \alpha$-$Al_2O_3$
1300	The same	$ZrO_2(t) + ZrO_2(m) + \alpha$-$Al_2O_3$ + $MgAl_2O_4$
1400	″	The same
1500	″	″
1600	″	″

When the mixtures were heated to 800 – 900°C, aluminum oxide existed in two phases (γ- and θ-) and at a temperature above 1100°C, the transformation of the crystalline cell of Al_2O_3 into α-corundum started. The fibers of partly stabilized zirconium dioxide consisted of the tetragonal phase with a small impurity of the monoclinic structure of ZrO_2. An increase in the temperature of heat treatment of the composites to 1300°C modified the ratio between the tetragonal and the monoclinic phases in zirconium dioxide. The amount of the latter increased due to partial disintegration of the ZrO_2 solid solution and the formation of alumino-magnesium spinel. However, complete disintegration of the solid solution did not happen. The modifications of the phase compositions of pure aluminum hydroxide gel and its fiber-containing composite after thermal treatment in the temperature range of 100 – 1600°C are indicated in Table 1.

The optimum filler composition should contain such quantity of a stabilizing additive that can ensure the content of the monoclinic and tetragonal zirconium dioxide structures in the composite in a certain ratio. In such case the transformation strengthening principle can be implemented in the ceramics [7].

In order to study the physicomechanical properties of the composites, square-shaped and cylindrical ceramics samples were produced, which contained the fibrous filler in the amount of 5, 10, and 20 wt.%. The samples were weighed, their geometrical sizes were measured before and after annealing at preset temperatures, and then the shrinkage and the weight loss were calculated. It was established that introduction of a fibrous filler has virtually no effect on shrinkage (18 – 19%) and weight loss (7 – 9%), but perceptibly modifies the density and strength of the material. The compressive and bending strength of ceramics based on pure aluminum hydroxide gel amounted to 250 and 180 MPa, and that of composites containing 20% filler was equal to 630 and 370 MPa.

Thus, the use of highly disperse fiber as the initial component for ceramics and the introduction of the fibrous filler into the gel matrix make it possible to obtain composite ceramics of increased strength. Under heat treatment of the ternary systems ($ZrO_2 – Al_2O_3 – MgO$), the component stabilizing the tetragonal structure of zirconium dioxide reacts with the aluminum oxide matrix and forms spinel interlayers on the fiber-matrix boundary. As a consequence, the solid solution of zirconium dioxide partly decomposes and four phases are formed within the system: tetragonal and monoclinic zirconium dioxide, α-corundum, and spinel. The impurity of the monoclinic phase of ZrO_2 (in accordance with the mechanism of microcrack formation) strengthens the material, and spinel forms additional bonds between the filler and the matrix in the composite, which improves the physicomechanical properties of the ceramics.

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